

BENEFICIATION OF A BITUMINOUS COAL AND A LIGNITE COAL
BY AGGLOMERATION USING NOVEL BINDING OILS.

R.C. Timpe, C.L. Knudson, P. Mack,

University of North Dakota Energy and Mineral Research Center
P. O. Box 8213, University Station
Grand Forks, ND 58202

ABSTRACT

Illinois #6 and both as received and hot water dried Zap (IndianHead) North Dakota lignite were agglomerated with Mandan refinery decant oil containing either p-xylene or deodorized rectisol naphtha from the Great Plains Gasification Plant. The effectiveness of each of the binding oils on agglomeration was determined from ash reduction and organic recovery as a function of mixing speed, mixing time, particle size, and oil-to-coal ratio. Results indicated that, although the ash reduction was significant in the Mandan decant/rectisol naphtha binder for both coals, greater reduction was achieved with the Mandan decant/p-xylene. Higher mixing speeds, longer mixing times, smaller particle size, and binder to coal ratio of 0.35 gave the greatest ash reductions. Agglomeration time was shortened substantially when either p-xylene or rectisol naphtha was added to the Mandan decant in place of using Mandan decant alone as binder.

INTRODUCTION

With the recent effort to educate the world's population on the wise use of the dwindling petroleum reserves and the associated emphasis on coal utilization, the world's supply of high quality, easily mined, low ash coal has also begun to dwindle.(1) Finding new, more efficient methods of beneficiation of higher ash coals has become a priority in coal research. Among the most widely used methods of fine coal beneficiation at present is froth flotation. Although the technique works quite well with higher rank coals and fines with larger particle sizes and low ash, it does have some drawbacks, among them comparatively low yield and high moisture content of product when fines are $<76\ \mu\text{m}$ and have high ash content. In addition, the lower rank, more readily mined coals and oxidized coal surfaces are not amenable to beneficiation by flotation. A promising complementary and possibly alternative technique is oil agglomeration.(2)

Agglomeration studies of lignite and subbituminous (low-rank) coals have not met with a great deal of success primarily because the experiments have centered around the successful techniques used to agglomerate bituminous coal. Since agglomeration is a surface phenomenon, the binding oil selected to form the aggregates of fines must be compatible with the surface functional groups on the fines. Most oils used for this purpose are oleophilic and as a result are readily adsorbed to the surface of the coal particles provided they have minimal polar groups exposed. This is characteristic of the bituminous coals but not of the lower rank coals. The subbituminous and lignite coals contain large amounts of surface oxygen making their surfaces more oleophobic than the bituminous. Since the theory of agglomeration assumes mineral material is considerably more hydrophilic and oleophobic than the organic coal matrix, the mineral material will dissolve or form a suspension in an aqueous medium and the organic matter will form aggregates and separate from that phase. Again, this is true for the coals of higher rank but not for the lower rank coals with their more polar, hydrophilic surfaces. The focus of this study was to investigate the agglomeration of a well behaved bituminous coal and a lignite coal when light organic compounds and lower value streams from a petroleum refinery and coal gasification plant are used as

binding oils. The reduction in ash content in the coal was studied as a function of particle size, mixing conditions, and oil characteristics.

In a successful agglomeration, the mineral content of the coal will be reduced significantly as the coal forms aggregates of organic rich material and the minerals are suspended in the aqueous phase. The degree to which a coal can be beneficiated by agglomeration is limited by several factors. The first is the particle size. The finer the particle size the more liquid solid surface contact and, consequently, the better are the chances of the carbonaceous material liberating its associated minerals thus lowering the ash content (3). Although fine grind enhances inorganics removal, it creates problems in handling the cleaned product and provides more area for undesirable surface reactions with oxygen. Effective agglomeration following ash reduction helps to solve these problems.

The second factor to be considered is the composition of the oil used as a binder. Light agglomerating oils (density < 0.90 g/cc) have been shown to give ash reductions in bituminous coals within 10 to 20 percent of those obtained with the Stoddard solvent (4). These oils, however, do not wet the surface of low rank coals well, and are not useful as binding oils for these coals. If heavier oils such as coke oven tars, pitches, and petroleum crudes are used, low-rank coals can be agglomerated, but these oils are more difficult to recover for reuse (4).

pH is a third consideration when carrying out agglomeration. Removal of most mineral material can be done with pH adjustment. However, with elements such as pyritic sulfur which is best removed at a pH between 7-11 the coal becomes more hydrophilic and agglomeration is less effective, requiring multiple pH adjustments to get maximum ash removal and agglomerate size and to reduce agglomeration time (1). Table 1 shows the ash content of the coal used in this study.

TABLE 1.
Agglomeration Test Coals

Sample	Mesh(70 wt %)	Ash mf(wt %)
Illinois #6	200	12.75
Illinois #6	325	24.85
Indian Head (AR)	325	14.63

The size of the agglomerates produced is a function of such processing variables as mixing speed, mixing time, mixer design, and solvent to coal ratio. Physical impact forces result in reduced agglomerate sizes with increased mixing speed and mixing time and contact with surfaces of smaller surface areas such as blade edges.(5) To minimize these impacts a blunt stir bar providing maximum contact area between agglomerates and bar is recommended. Thorough agitation may increase the yield but not necessarily the size of the agglomerates. Increasing the ratio of binding oil to coal tends to increase agglomerate size, making binding oil recovery an economically important aspect of this method of beneficiation (6). Recovery of 40 to 50% of the binding oil by thermal treatment under reduced pressure maintains the calorific value of the product, decreases the moisture content, increases mechanical stability, and results in reduction of selfignition hazards.

EXPERIMENTAL

Agglomeration tests were carried out on as-received Illinois #6 bituminous coal and an as-received and a hot water dried North Dakota lignite from the Indian Head mine. The coals were ground to 70 wt% 200 mesh (75 μ m) and 325 mesh (45 μ m).

The percent ash values on a moisture free basis are shown in Table 1.

Screening tests were carried on nine different liquids to determine the most suitable binding oil for agglomerating the test coals. The oils tested included Lummus Arabian and Lloydminster petroleum resids, North Slope ATB, Mandan Decant oil, Mayan crude, rectisol naphtha, JP4 aviation fuel, 1 octanol, and p-xylene. The Mandan crude exhibited better agglomerating results than the other oils for both the bituminous and the lignite coals. The binding oils selected for this study were Mandan Decant oil (MDO) from the Amoco refinery at Mandan, North Dakota, and mixtures of MDO with p-xylene (MDO/XY) or rectisol naphtha (MDO/RN) from the Great Plains Gasification Plant at Beulah, North Dakota. The solvent mixtures were 50 wt % Mandan Decant oil in either p-xylene or rectisol naphtha.

The laboratory experiments were carried out in both large and small scale mixers. The small scale experiments (called micro agglomeration) consisted of stirring 0.50 g coal, 0.15 to 0.35 g of oil, and 10 g H₂O at 10,000 to 21,000 revolutions per minute (rpm) in a micro-agglomeration cell for measured time periods.

A variable speed blender with a fabricated bar propeller stirring rod was used to carry out the larger scale experiments. Five hundred ml of deionized water was poured into a stainless steel mixing cup. The weighed binding oil was poured into the cup and the oil and water mixture was stirred at 10,000-20,000 rpm for several minutes prior to introducing the weighed coal sample into the unstirred mixture. The water, oil, and coal was stirred at the above rate for from 1 to 6 minutes.

Following the stirring, the inherent pH of the slurry was measured using pH paper. (The effect of pH adjustment on the agglomeration was not included as part of the study reported here but instead is included in the work currently underway.) The slurry was then poured over a 100 mesh screen to collect the agglomerates. 500 ml of deionized water was used to rinse the agglomerates and then they were extracted with 100 ml tetrahydrofuran (THF), filtered under vacuum, and air dried over night. Moisture and ash content were then determined.

RESULTS AND DISCUSSION

The initial experiments were carried out with Mandan decant oil p-xylene on the Illinois #6 bituminous coal since previous agglomeration work has been successful with this coal rank. Micro- and large-scale agglomeration experiments produced agglomerates which differed in size and texture with different solvent to coal ratios, mixing speeds and mixing times. A satisfactory solvent to coal ratio for agglomeration of the bituminous coal with Mandan decant oil was determined by first investigating the agglomerating properties of the oil itself and then by comparing those properties with those of dilutions of decant oil with p-xylene. Rectisol naphtha, a light oil stream obtained from the commercial coal gasification plant at Beulah, North Dakota, was substituted for the p-xylene in some of the later experiments. The ash content of the agglomerates formed in this solvent was determined and compared with that of agglomerates formed at the same conditions using the MDO p-xylene.

The characteristics of the agglomerates apparent to the eye are described in terms of size and texture. Micro-agglomerates or flocs are the smallest, discrete are "medium sized", and amalgams are the large coal-in-oil pastes. The texture is either firm or loose. Tables 2 and 3 show the characteristics of agglomerates formed at a variety of conditions for both the bituminous and the lignite coal. The series of experiments carried out with Mandan Decant oil to determine its agglomerating ability gave the desired firm amalgam at a minimum solvent to coal ratio of 0.6 when allowed to stand overnight. Sun and McMorris

reported that high specific gravity oils do not disperse well enough in coal slurry to wet the coal (1). Since MDO has a specific gravity of 1.0202 (considered high), accounting for the slow formation of agglomerates, lower specific gravity organic liquids were added to reduce it to the medium range. A 50 wt % MDO in p-xylene gave a medium range specific gravity of 0.9400 and this binding oil agglomerated the 325 mesh bituminous coal sample within minutes at a solvent to coal ratio of 0.7 when stirred for 3 minutes at 10000 rpm. The larger 200 mesh particles formed firm agglomerates at a solvent to coal ratio of 0.5 under the same stirring conditions.

TABLE 2.

MICROAGGLOMERATION RESULTS FOR 325 MESH ILLINOIS #6 BITUMINOUS
"COAL, AS RECEIVED

Binding Oil	Solvent/Coal Ratio	Speed (rpm)	Mixing		Agglomerates Type Texture	
			Time(min) Solvent	Time(min) Slurry		
Illinois #6 Bituminous						
MDO	0.4	10,000	1	3	floc	loose
MDO	0.5	10,000	1	3	floc	loose
MDO	0.6*	10,000	1	3	amal	firm
MDO	0.7	10,000	1	3	disc	loose
MDO/XY	0.5	10,000	1	3	disc.	firm
MDO/XY	0.6	10,000	1	3	disc.	firm
MDO/XY	0.7	10,000	1	3	amal.	firm
MDO/XY	0.5	10,000	2	3	amal.	firm
MDO/XY	0.6	10,000	2	3	amal.	firm
MDO/XY	0.7	10,000	2	3	amal.	firm
MDO/XY	0.8	10,000	2	3	none	--
India Head Lignite						
MDO/XY	0.30	10,000	2	3	floc	firm
MDO/XY	0.40	10,000	2	3	disc.	firm
MDO/XY	0.50	10,000	2	3	disc.	firm
MDO/XY	0.60	10,000	2	3	disc.	firm
MDO/XY	0.70	10,000	2	3	disc.	firm
Hot Water Dried Indian Head Lignite						
MDO/XY	0.30	10,000	2	3	disc.	firm
MDO/XY	0.40	10,000	2	3	amal.	firm
MDO/XY	0.50	10,000	2	3	amal.	firm
MDO/XY	0.30	20,000	2	3	disc.	firm
MDO/XY	0.40	20,000	2	3	disc.	firm
MDO/XY	0.50	20,000	2	3	amal.	firm

MDO/XY = 50 wt % MDO in XY

MDO = Mandan Decant Oil

XY = p-xylene

floc = micro-agglomerates

disc = discrete agglomerates

amal=amalgams

*agglomerates formed
overnight

Table 4 shows the results in terms of product ash content of experiments carried out on the larger unit. Simple calculation from this table shows the ash reduction of the 325 mesh bituminous coal was greater than that of the 200 mesh samples. This is not unexpected in light of the fact that the smaller particles have more surface contact with the oil. Experiments with the 200 mesh bituminous

coal on the larger scale unit showed that firm amalgams could be formed at a ratio of as low as 0.3 when stirred for 6 minutes at 13,000 rpm resulting in an ash reduction of 8%. Although these particles are more easily handled physically, Table 4 shows that greater ash reduction is accomplished in forming the smaller particles.

TABLE 3.
MICROAGGLOMERATION RESULTS FOR 70 wt % 200
MESH ILLINOIS BITUMINOUS COAL, AS RECEIVED

Binding Oil	Solvent/Coal Ratio	Speed (rpm)	Mixing		Agglomerates Type Texture	
			Time(min) Solvent	Time(min) Slurry		
MDO/XY	0.5	10,000	2	3	amal.	firm
MDO/XY	0.6	10,000	2	3	amal.	firm
MDO/XY	0.7	10,000	2	3	amal.	firm

The same solvent as in the experiments with the bituminous coal was used in the experiments with the Indian Head lignite. In the micro agglomeration tests with 325 mesh asreceived lignite at solvent to coal ratios of 0.25-0.70 and stirring rates of 10,000 rpm for 3 minutes no firm amalgams were formed. However, under identical conditions hot water dried lignite formed firm amalgams at solvent to coal ratios of 0.40, and at similar conditions but with a stirring rate of 20,000 rpm, amalgams formed in a solvent to coal ratio of 0.50. In large scale tests, the as received lignite formed only firm discrete agglomerates. With hot water dried lignite firm amalgams were formed in the MDO p-xylene when mixing at 10,000 rpm for 3 minutes in a solvent to coal ratio of 0.25 and resulted in a 21% reduction in ash content. Firm amalgams were also formed at ratios of 0.30, 0.35, and 0.40 at the same mixing speed and time conditions with nominally 8% reduction in ash. Increasing the mixing speed to 20,000 rpm resulted in firm amalgams at a ratio of 0.30 with a 14% reduction in ash. Substitution of the rectisol naphtha for the p-xylene in the solvent mixture was found to yield only firm discrete particles and the most satisfactory solvent to coal ratio was 0.40. The ash reduction was 13% as compared with a reduction of 17% with the MDO p-xylene at the same mixing conditions.

The pH was determined to be ~6 for the slurries included in this study. Current work getting underway includes a study of the effect of adjusting the pH to enhance agglomeration and ash reduction.

CONCLUSIONS

The following conclusions are suggested by the data:

- o Mandan Decant Oil, a high density oil, will agglomerate the studied coal types only after standing for extended periods of time, while a 50 wt % mixture of MDO in either p-xylene or rectisol naphtha, which forms a medium density oil, will agglomerate these coals within several minutes.
- o Hot water drying of lignite enhances its agglomerating properties.
- o Agglomerates which are flocculate or discrete in form generally gave higher ash reductions than amalgam agglomerates.
- o Higher mixing speeds and longer mixing times although not giving large agglomerates, generally gave higher ash reductions with both coals studied.

- o The MDO/XY binder caused greater reduction of the ash content of the 325 mesh as received lignite (17%) than the MDO/RN (13%).
- o Agglomerate formation is dependent on the design of the stirrer.
- o When using the MDO/XY solvent, the ash content of the 325 mesh bituminous coal was reduced more than that of the 200 mesh coal, showing reductions of 17% and 14% respectively. A 14% reduction in ash was realized for the 325 mesh hot water dried lignite as compared to 12% for the as received lignite.

TABLE 4.

AGGLOMERATION RESULTS FOR A 50 WT % MANDAN DECANT OIL
IN P-XYLENE OR RECTISOL NAPHTHA.

Solvent/Coal Ratio	Speed (rpm)	Time(min) Solvent	Time(min) Slurry	Agglomerates Type Texture		Product % Ash •
200 Mesh Illinois #6 Bituminous, as received						
0.30	13,000	2	3	disc.	firm	11.75
0.35	13,000	2	3	disc.	firm	10.91
0.40	13,000	2	3	amal.	loose	11.05
0.25	13,000	2	6	disc.	firm	11.97
0.30	13,000	2	6	amal.	firm	11.69
0.35	13,000	2	6	amal.	firm	11.37
0.25	16,000	2	6	disc.	firm	11.25
0.30	16,000	2	6	disc.	firm	11.07
0.35	16,000	2	6	disc.	firm	10.96
325 Mesh Illinois #6 Bituminous, as received						
0.25	16,000	2	6	floc	firm	21.83
0.30	16,000	2	6	floc	firm	20.99
0.35	16,000	2	6	disc.	firm	20.55
325 Mesh Indian Head Lignite, as received						
0.40 MDO/XY	15,000	2	6	disc.	firm	12.09
0.40 MDO/RN	15,000	2	6	disc.	firm	12.72
325 Mesh Hot Water Dried Indian Head Lignite						
0.25	10,000	2	3	amal.	firm	8.73
0.30	10,000	2	3	amal.	firm	10.29
0.35	10,000	2	3	amal.	firm	10.12
0.40	10,000	2	3	amal.	firm	10.27
0.30	20,000	2	3	amal.	firm	9.49
0.35	20,000	2	3	disc.	firm	9.44
0.40	20,000	2	3	disc.	firm	9.58

*Moisture free basis.

MDO/XY = 50 wt % Mandan Decant Oil in p-xylene

MDO/RN = 50 wt % Mandan Decant Oil in rectisol naphtha

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